

PATENT SPECIFICATION

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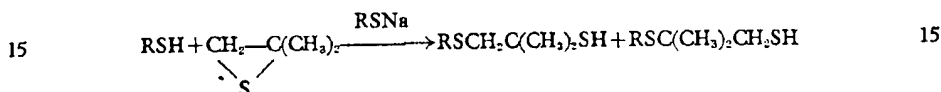


(54) POLYTHIOETHERS FORMED BY ANIONIC RING OPENING OF EPISULFIDES

(71) We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

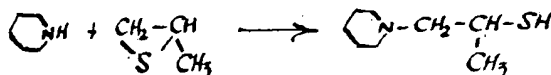
This invention relates to a selective anionic ring opening process which comprises reacting episulfides with thiols in the presence of certain catalysts. More specifically, this invention relates to polyfunctional polythioether thiols and polythiols which are derived by the process of this invention which are suitable as mastics and rubbers and may be readily crosslinked by conventional techniques.

Anionic ring opening reactions of episulfides are known. For example, U.S. patents 2,490,984 and 2,497,100 describe the nonselective anionic ring opening of episulfides by thiols in the presence of sodium thiolates as catalysts, e.g.



wherein R is an alkyl group.

The anionic ring opening of episulfides by primary and secondary amines is also known. The reaction was reviewed in some detail by M. Sander (see Chemical Reviews, vol. 66, pp. 331—333, year 1966). For example, A. Oddon and J. Wylde reported that secondary amines selectively open the propylene episulfide ring via an anionic mechanism to form the corresponding secondary aminoethanethiols; e.g.,



Cf. Bull. Soc. Chim., France 1967, pp. 1603—1607.

The ring opening of episulfides by thiols in the absence of catalysts is known (see German Patent 696,774). However, such reactions require higher temperatures.

It has surprisingly been found that thioetherthiols may be prepared via the amine or phosphine catalyzed ring opening of episulfides by thiols. Where the thiol is a polythiol, the reaction products are polyfunctional polythioetherthiols.

The monothioetherthiols of the invention are useful as intermediates for the synthesis of pesticides. The polythioether dithiols and polythiols are suitable for use as mastics and rubbers.

The preferred episulfides are ethylene episulfide and propylene episulfide. Where the episulfide is an unsymmetrical episulfide, e.g. propylene episulfide, the resultant product is the thiol isomer which is more highly substituted at the alpha-carbon atom.

In accordance with this invention, episulfides are reacted with thiol compounds, the reaction being catalyzed by organic phosphine catalysts to form thioether thiols

[Price 25p]

and phosphine complexes thereof. In certain circumstances as hereinafter defined organic amines can be used as catalyst.

Among the episulfides suitable for use in the practice of this invention are those episulfides having the general formula:



wherein R' , R'' and R''' are hydrogen, hydrocarbyl radicals and substituted hydrocarbyl radicals. In a preferred embodiment R'' and R''' are hydrogen, C_1 — C_{20} hydrocarbyl radicals or C_1 — C_{20} substituted hydrocarbyl radicals; preferably R'' and R''' are C_1 — C_6 alkyl, C_1 — C_6 cycloalkyl, phenyl or tolyl; more preferably R'' and R''' are hydrogen, methyl or ethyl; most preferably R'' and R''' are both hydrogen. R' as defined above comprises C_1 to about $C_{200,000}$ radicals; more preferably a C_1 to C_{20} radical; more preferably R' is a C_1 — C_{16} hydrocarbyl radical; e.g. C_1 — C_6 alkyl, allyl or propargyl. For example, R' may be ethyl or methyl.

The term C_1 — C_{20} hydrocarbyl radical includes acyclic, alicyclic or aromatic and the acyclic or alicyclic radicals may be either saturated, unsaturated, linear or branched radicals. The alicyclic radicals may be single ring, bridged or fused ring compounds.

Illustrative examples of these C_1 to C_{20} hydrocarbyl radicals are methyl, propyl, isopropyl, secondary amyl, tertiary amyl, vinyl, propenyl, hexenyl, cyclobutyl, cyclohexyl, norbornyl, tetrahydroindyl, alkyl substituted derivatives of these alicyclic compounds, phenyl, naphthyl, anthranyl, aralkyl, etc.

The substituents of the R' hydrocarbyl radical can be hydroxy, hydrocarbyloxy, hydrocarbylthio, acyl, thioketonic, alkylene sulfide, polyester alkylene oxide or hydrocarbylene polyether groups. When used in the specification and claims, the term "substituted hydrocarbyl radical" means the hydrocarbyl radicals disclosed herein substituted with one or more of the aforementioned substituents. The hydrocarbylene polyether group can be a polyalkylene oxide, a polyalkylene sulfide, a polyalkylene polysulfide.

The term "unsymmetrical episulfide" means an episulfide wherein R' , R'' and R''' are not the same, for example where R'' and R''' are hydrogen and R' is a C_1 to C_6 alkyl or cycloalkyl radical. The term "mono-substituted episulfide" means an episulfide wherein at least two of the groups R' , R'' or R''' are hydrogen and the other is as previously defined but not hydrogen.

Illustrative of the episulfides suitable for use in the practice of this invention are ethylene sulfide, propylene sulfide, butadiene monosulfide, dodecene sulfide, dotriacontene sulfide, cyclohexene sulfide, styrene sulfide, stilbene sulfide, polybutadiene sulfide, 3-hydroxy-propylene sulfide, 3-allyloxypropylene sulfide, 3-phenylthiopropylene sulfide, 3-dichlorophenoxythiopropylene sulfide, 3-acetylthiopropylene sulfide, 3-diethoxythiophosphorylthio-propylene sulfide, diallyl polytrimethylenethioether sulfide, N-phthalimidopropylene sulfide, etc. Preferred of these are ethylene sulfide and propylene sulfide.

The thiol reactants suitable for use in the practice of this invention are represented by the general formula:



wherein R is hydrogen or an organic radical, preferably R is an organic radical of about C_1 to $C_{200,000}$ carbon atoms, more preferably, R is a hydrocarbyl radical or substituted hydrocarbyl radical; and m is an integer representing the valency of R . Preferably m varies from 1 to 500, for instance from 1 to 50, e.g. 2 to 10; most preferably m is 1 to 10, e.g. 1 to 4.

In a preferred embodiment, R is a hydrocarbon or substituted aliphatic hydrocarbon radical, more preferably a substituted aliphatic radical. The substituents on the radical can be oxy, thio-ether groups, ester groups, halogenated aromatic groups, dialkyl amino groups, etc. Both oxygen and sulfur may be present in the same radical. The oxygen or sulfur may exist as ether or carbonyl groups and thioether or thioketone groups, respectively. For example, R can be a polyalkylene thioether radical wherein the hydrocarbon chain is interrupted by sulfur atoms. R can however be a heterocyclic organic radical containing sulphur or oxygen. The aliphatic radical can

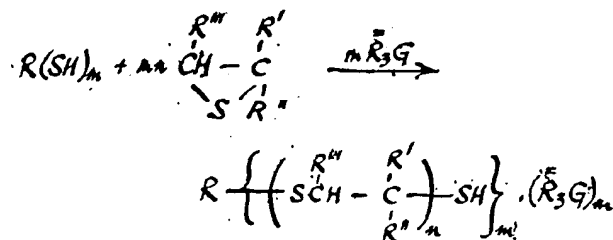
be a primary, secondary or tertiary radical. In an embodiment of this invention, R is an organic radical containing 1 to 1,000 carbons, preferably, it is a C_1 to C_{100} radical, more preferably a C_1 — C_{30} radical; most preferably R is a hydrocarbon radical of preferably 1 to 30 carbon atoms, C_2 to C_{12} , e.g. a C_1 to C_{30} aliphatic hydrocarbon radical. Ideally R is an aliphatic hydrocarbon radical of 1 to 10 carbon atoms; preferably 1 to 6 carbon atoms and m is less than 4, e.g. 3. Where R is H, m must be 1 and the compound is H_2S . Where m is 1 and R is an organic radical, the reactant is a monothiol. Where m is 2 or 3, the thiol is di- or tri-thiol, respectively. The thiol can for example be a C_1 to C_{30} hydrocarbyl or C_1 to C_{30} substituted hydrocarbyl thiol or a C_2 to C_n alkylene dithiol.

Aliphatic polythiols, e.g. dithiols are the preferred polythiols of this invention. Illustrative examples of the thiols suitable for use in the practice of this invention are: Monothiols: methanethiol, n-butanethiol, i-propanethiol, t-dodecanethiol, dotriacontane thiol, polyethylene thiol, hydroxyethanethiol, carboethoxymethanethiol, cyanoethanethiol, 5-hexenethiol, cyclopentanethiol, chlorobenzenethiol, dinitrobenzenethiol, 2-benzothiazolethiol, alpha-toluenethiol, polyethylenesulfidethiol, t-butylthioethanethiol. Dithiols: ethanedithiol, 1,3-propanedithiol, 1,4-butanedithiol, hexamethylene dithiol, dotriacontanedithiol, cyclohexanedithiol, benzene-dithiol, xylenedithiol, polymethylenedithiol, polypropylene-sulfidethiol, ethylene-bis-oxyethanethiol, diphenylsulfide-dithiol, bis-methylenecarboalkoxyethanethiol, 3-hydroxypropanedithiol. Polythiols: propanetrithiol, benzenetrithiol, beta,beta,beta-triethylcyclohexanetrithiol, cyclododecanetrithiol, polybutadienepolythiol, polypropylenesulfide polythiol, octanetrithiol, dodecanetetrathiol, hexadecanepentathiol, trimercaptopropionyltriazine, tetra-mercaptoethyl silane, tri-mercaptopropyl phosphate, trimethylol propane trimercaptopropionate, tri-mercaptopropyl carbinol, polyethylenemaleate polythiol, pentaerythritol tetra-mercaptopropionate.

The term "organic thiols" as used in the specification and claims means the monothiols, dithiols and polythiols used as reactants in this invention and includes H_2S as a monothiol.

The synthesis of the starting hydrocarbon trithiols and polythiols is often expensive. A preferred method of trithiol and polythiol synthesis uses the addition of excess hydrogen sulfide to a thiolefin or polyolefin. The resulting polythioether polythiols can be used as advantageous starting materials for the present synthesis. Similarly, the polythiol adducts of hydrogen sulfide to triacryloyl triazine, triacryloyl ester, triallylcarbinol, etc., can be used.

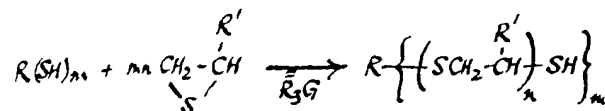
The reaction of thiols with the episulfides according to the process of this invention is represented by the general equation:



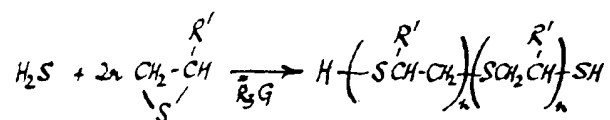
wherein R, R', R'', R''' are as previously defined, \bar{R} is hydrogen, a C_1 to C_{30} hydrocarbyl radical, C_1 — C_{30} substituted hydrocarbyl radical, G is phosphorus, and m and

n are integers of 1 or greater. \bar{R} is preferably a C_1 to C_6 alkyl group. In carrying out the reaction, it is not essential that the catalyst and thiol be present in equimolar quantities based on this thiol functionality.

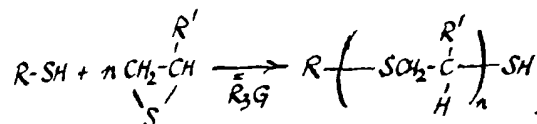
Where R'' and R''' of the episulfide are hydrogen, the reaction is represented by the equation:



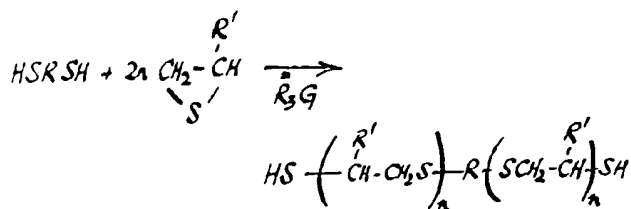
where the thiol compound is H_2S , the reaction may be represented as follows:



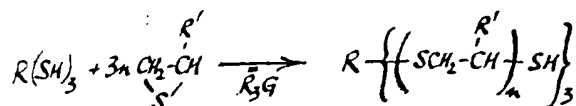
Similarly, the reaction of mono, di and trithiols with the episulfides of this invention is represented by the equation:



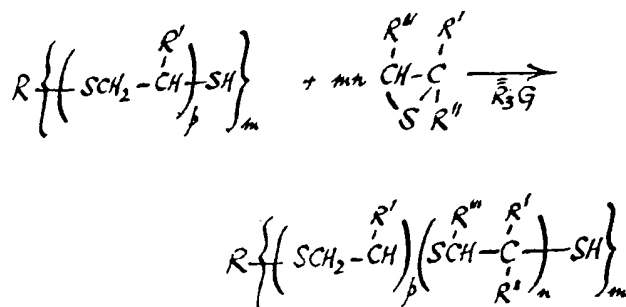
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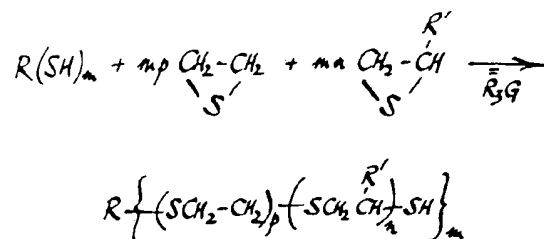
If desired, a mixture of various episulfides may be coreacted with the thiol compound. The polythioether polythiol products of the present invention can be further reacted with an episulfide different from the ones used in their preparation.



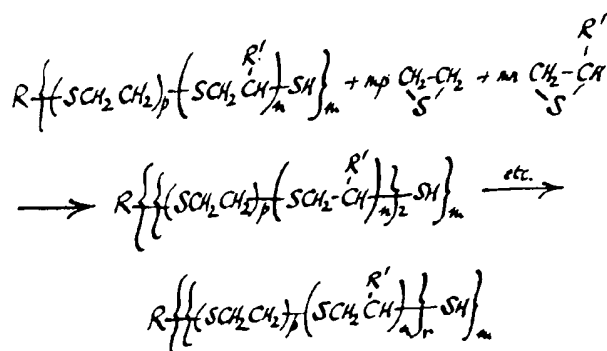
10 wherein the meaning of the previously used symbols is the same and p is a number of 1 to 20,000.

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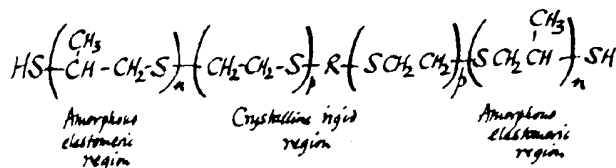
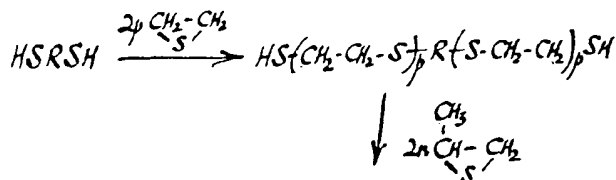
The same type of sequential reaction can be carried out using a mixture of ethylene episulfide and a less reactive substituted derivative.



After the original episulfide mixture reacts, a new mixture can be added to form further blocks of the polymer. This procedure can be repeated at will. The resulting transformations are shown by the following reaction scheme.

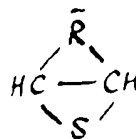


wherein r is an integer equivalent to the number of times the step is repeated; preferably r is less than 10. A particularly advantageous feature of the present process is the possibility of stepwise reactions to form linear polymers having both amorphous aliphatic regions and crystalline regions. For example, these block polymers may be prepared by reacting dithiols with ethylene episulfide and then further reaction of the product with propylene episulfide. The reaction is described by the following equation:

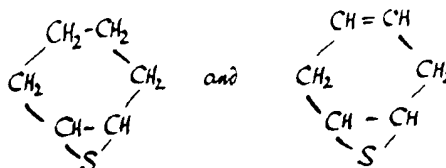


Instead of propylene episulfide, other alkyl substituted ethylene sulfides of increased reactivity can be also used for the preparation of similar block copolymers.

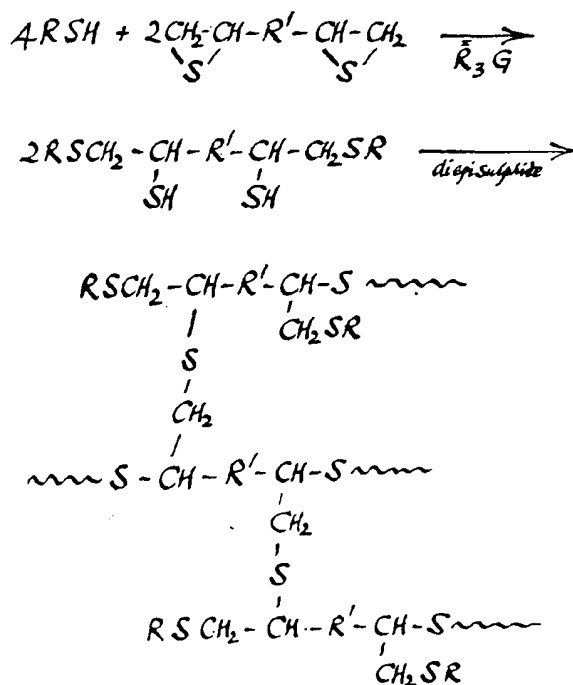
Although the episulfides of this invention have been generally described as linear or branched chain episulfides, compounds having cyclic constituents may be used. These compounds have the general formula:



- 5 wherein \bar{R} is a C_2 — C_{10} alkylene or C_2 — C_{10} alkenyl radical. For example, illustrations of compounds wherein \bar{R} is C_4 are:



Polyfunctional episulfides may also be used in the practice of this invention. These compounds of course react to form highly crosslinked networks, e.g.



crosslinked network

R' may be a divalent hydrocarbyl or substituted hydrocarbyl radical of about 1 to 20 carbon atoms. Preferably, R' is a C_2 to C_8 alkylene radical.

- 15 Polymeric compositions such as polybutadiene may be modified to have pendant of the backbone episulfide groups. These polymers may be crosslinked by reaction with polythiols. A preferred polythiol is prepared by reacting polybutadiene with

H₂S in the presence of a free radical catalyst. The reaction is preferably carried out in an excess of H₂S.

The reactions of this invention are carried out in the presence of an organic phosphine catalyst, and if reacting more than one episulphide, an organic amine can be used as an alternative catalyst. The amines or phosphines can be cyclic compounds containing one or more nitrogen or phosphorus atoms. For example, tertiary heterocyclic nitrogen compounds such as pyridine or triethylene diamine may be used. The use of an organic amine as catalyst results in the formation of new compounds which are secondary and tertiary thioether diols, triols and polyols as hereinafter defined.

The preferred amine catalysts of this invention may be represented by the schematic formula $\overline{\text{NR}}^{\overline{\text{m}}}$, wherein $\overline{\text{s}}$ is an integer of 1, 2 or 3 and $\overline{\text{R}}$ is hydrogen, a C₁ to C₃₀ hydrocarbyl radical or a C₁ to C₃₀ substituted hydrocarbyl radical; preferably a C₁ to C₁₂ hydrocarbyl radical; more preferably a C₁ to C₆ hydrocarbyl radical;

most preferably, $\overline{\text{R}}$ is a C₁ to C₁₂ aliphatic hydrocarbyl radical, more preferably a C₁ to C₆ aliphatic hydrocarbyl radical; $\overline{\text{R}}$ can be C₁ to C₁₀ alkyl, C₁ to C₁₀ alicyclic hydrocarbyl radicals or mixtures thereof, e.g. cycloalkylene or cycloalkylidene.

It will be evident that where $\overline{\text{s}}$ is less than 3, at least one $\overline{\text{R}}$ is a cyclic radical. For example, where $\overline{\text{s}}$ is 2, the compound may be N-ethyl piperidine; where $\overline{\text{s}}$ is 1, the compound may be pyridine. The cyclic amines may be alkyl substituted in one or more positions, said alkyl groups containing 1 to 6 carbon atoms. Illustrative examples of the $\overline{\text{R}}$ radical are methyl, propyl, hexyl, amyl, octyl, isooctyl, dodecyl, cyclohexylene, cyclohexylidene, etc.

It will be evident that where $\overline{\text{s}}$ is 1, the compound is a heterocyclic compound such as pyridine; where $\overline{\text{s}}$ is 2, the compound is a cyclic compound such as N-ethylpiperidine; where $\overline{\text{s}}$ is 3, the compound is a triorgano amine. Preferably, $\overline{\text{s}}$ is 3 and $\overline{\text{R}}$ is a C₁ to C₆ hydrocarbyl radical; more preferably $\overline{\text{R}}$ is a C₁ to C₆ alkyl or alkenyl radical; most preferably $\overline{\text{R}}$ is methyl, ethyl, propyl or butyl.

Where the amine or phosphine is a triorgano compound, it may be represented by the general formula $\overline{\text{R}}_3\text{G}$ wherein $\overline{\text{R}}$ is a C₁ to C₃₀ hydrocarbyl radical or a C₁ to C₃₀ substituted hydrocarbyl radicals and G is N or P. Preferably, $\overline{\text{R}}$ is a C₁—C₆ aliphatic radical, most preferably, $\overline{\text{R}}$ is a C₁—C₄ alkyl radical. $\overline{\text{R}}$ may also be a C₄—C₆ cycloalkyl group.

Illustrative of the amine catalyst which may in certain circumstances be used in the process of this invention are trialkyl amines such as trimethylamine, hexadecyldimethylamine, didodecylmethylamine, quinuclidine, methylethylhexylamine, tri-*i*-propylamine, triethanolamine, triallylamine, tripropargylamine, dimethylbenzylamine, N-methyl piperidine, N-methylmorpholine; bis-amines such as N,N'-dimethylpiperazine, tetramethylethylenediamine, triethylenediamine, hexamethylene tetramine, alpha, alpha'-dimethyldotriacontylamine, pentamethyldiethylenetriamine, pyridine, quinoline, N-methyl imidazole, N-ethyl piperidine, pyrazine, quinoxaline, thiazole; dimethyl amine, diisopropyl amine, ethyl hexyl amine, methyl dodecyl amine, diethanol amine morpholine; primary amines such as ethyl amine, hexyl amine, dodecyl amine, docosylamine, tricontyl amine, ethanol amine, hydroxypropyl amine, ethyl aminopropionate, monoamino acetone.

Illustrative examples of tertiary organophosphines which may be used as catalyst are trimethyl phosphine, tributyl phosphine, tridecyl phosphine, diethylhexyl phosphine, P-ethylphosphetane, triallyl phosphine, dimethylcyclohexyl phosphine, tetramethyl ethylene diphosphine.

The present selective ring opening process is highly advantageous for the production of novel polythioethers having secondary thiol end groups. By using several episulfides in the process, polythioether block copolymers having crystalline and elastomeric segments are prepared. By substituting polythiols for monothiols, poly-

thioether polythiols are derived. The reactive terminal functionality of the latter is advantageous for castable rubber applications and the like.

The polymerization of the thiol in the catalyst complex is dependent on both the thiol and the catalyst. The higher the thiol's acidity, the greater is the anionic character of the complex. Due to their greater anionic character, amine complexes of aromatic thiols show higher reactivities than those of the aliphatic thiols. The basicity of the catalyst is also directly related to the reactivity of the complex; therefore, aliphatic amines are preferred to the aromatic amines. Bicyclic aliphatic amines with an exposed unshared electron pair on the nitrogen such as triethylenediamine are particularly effective catalysts because of the reduced steric crowding.

The effectiveness of the catalyst will be, of course, also dependent on the episulfide reactant. Ethylene episulfide, for example, shows a much higher reactivity than propylene episulfide.

The ratio of tertiary amine catalyst to thiol is not critical. In general, higher ratios result in greater reaction rates. Amine catalysts can be used in quantities ranging from about .01 moles or more per mole of thiol reactant; preferably, about 0.01 to about 2 moles per mole of thiol reactant; more preferably .05 to about 1.5 moles; most preferably about 0.1 to about 1 mole.

The ratio of episulfide to thiol reactants will determine the molecular weight of the product. The lesser the amount of thiol reactant used, the higher the molecular weight of the resultant product. The episulfide reactant to thiol ratio is not critical. It can be as little as .005; preferably about 0.005 to about 10,000; more preferably, about 1 to 2000; most preferably from 0.5 to 1000. For the preparation of monothioetherthiols from episulfide-monothiol reactions, reactant ratios of about .5 to 2 are preferred. For the synthesis of polythioether thiols, thiol compounds, i.e., di- or polythiols, are reacted with approximately the number of episulfide molecules per thiol one desires to link up by ring opening into a macromolecule.

The reactions of this invention can be carried out at any convenient temperature. The preferred range is about -100°C to $+150^{\circ}\text{C}$. The higher temperatures favor the ring opening of the episulfide; however, they reduce the hydrogen bonding between the thiol and the amine and therefore diminish the activity of the amine catalyst. Consequently, the lower temperatures are preferred in the practice of this invention. More preferably, the reaction is carried out at 0° to 120°C , most preferably 20° to 70°C , e.g., 25 to 40°C .

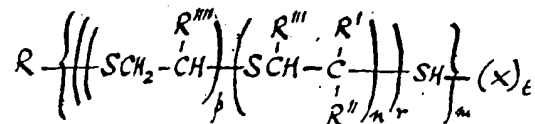
The pressure at which the reaction is carried out is not critical; however, it should be sufficient to maintain all of the reactants in the liquid phase at the elevated temperatures. Supercritical pressures may be necessary. The preferred pressure range is about 1 atmosphere to 50 atmospheres, more preferably about 1 atmosphere to 10 atmospheres.

Although solvents are not necessary for the reactions since the episulfides themselves are liquids, solvents may be used to control the reaction temperature and in the case of solid products, maintain the reaction system in a homogeneous liquid state. Any solvent which is a solvent for the episulfides and the products and does not react with the amine or episulfides is suitable. Any excess of tertiary amine may be used as a solvent. However, the preferred solvents are aromatic hydrocarbons, thioethers, chlorinated aromatic hydrocarbons, N,N-dialkylamides and esters. The ethylene episulfides and propylene episulfides may be used in excess as solvents also.

Illustrative examples of the solvents which may be used in the practice of this invention are toluene, diethyl sulfide, chlorobenzene, dimethyl formamide, ethyl acetate, diethyl sulfone, thiophene, ethanol, etc.

Solvents in which some reactants and/or products are insoluble can be advantageously used to make the higher molecular weight polythioether products of this invention, for example, by emulsion polymerization. Suitable media for such systems include water, methanol, cyclohexane, tetrahydrofuran, methyl ethyl ketone, etc.

The present novel process provided new compounds, i.e., secondary and tertiary thioether dithiols, trithiols and polythiols of the general formula:

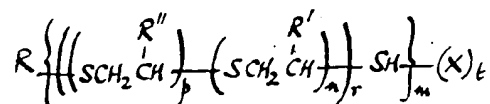


R, m and r are as previously defined; X is an organo amine or an organo phosphine; R'' and R''' and R'''' are independently hydrogen, or a C₁ to C₆₀ nonsub-

stituted or substituted hydrocarbon radical, preferably an alkyl radical or hydrogen, most preferably hydrogen, methyl or ethyl. If R'' is hydrogen, R''' must also be a hydrogen. Also when R'' and R''' are both hydrogen R' cannot be the same as R'''. Preferably R''' is hydrogen or a C₁ to C₄ aliphatic hydrocarbon radical such as alkyl, allyl or propargyl; more preferably, R''' is hydrogen or methyl. Most preferably, R''' is hydrogen. R' is a substituted or nonsubstituted monovalent hydrocarbon radicals in the C₁ to C_{200,000} preferably in the C₁ to C₃₀ range, e.g. C₁ to C₄. More preferably, R' is a C₁ to C₁₀ open chain aliphatic hydrocarbyl radical, especially a C₁ to C₄ alkyl, allyl or propargyl radical. The symbol n is an integer of 1 to 50,000, preferably 1 to 20,000, more preferably 2 to 3000, most preferably 3 to 1000; p represents a number of 1 to 20,000, e.g. 1 to 10,000, more preferably 0 to 3000, most preferably 1 to 1000. r is 1 to 10, e.g. 2 or 3, preferably 1. t is 0 or a number of 0.01 to 10, preferably 0 to 3. Where t is 0, the uncomplexed thiol terminated thioether is produced. Where t is an integer, the compound is the thiol complexed with the catalyst. Since the thiol may be a polythiol and the catalyst may be used in quantities less than equimolar with respect to the thiol, t need not be an integer. Preferably t is 0 to 5; more preferably t is 0.

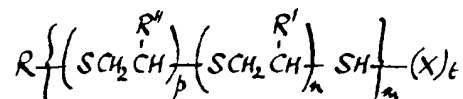
The term "thioether thiol compound" as used in the specification and claims means both the uncomplexed thiol and the thiol complexed with the catalyst of this invention.

In a more specific embodiment such compounds include those of the general formula



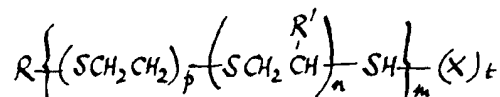
wherein the meaning of symbols is as previously defined.

More specifically such compounds include those of the formula



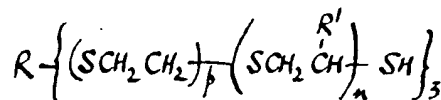
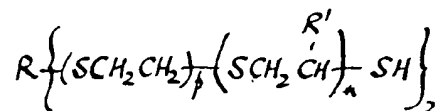
wherein the meaning of symbols is the same.

Most specifically such compounds include those having the formula



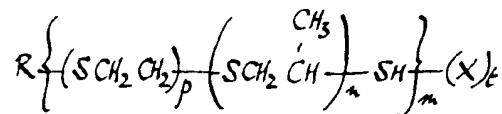
wherein the symbols have the meaning specified before.

In other specific embodiments such compounds include those of the formula



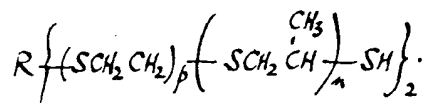
wherein the symbols have the same meaning as specified earlier. R² and R³ represent di- and trivalent radicals respectively.

The new compounds include those of the general formula

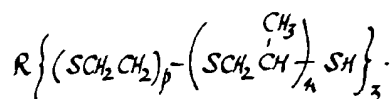


wherein the meaning of R and (X), is as previously defined; m is 2 to 50, preferably 1 to 10, more preferably 3; n is 2 to 50,000, preferably 2 to 20,000, more preferably 2 to 3000, most preferably 3 to 1000; p is 1 to 20,000, preferably 1 to 20,000, more preferably 1 to 3000, most preferably 1 to 10,000.

These compounds include compounds of the formula



and

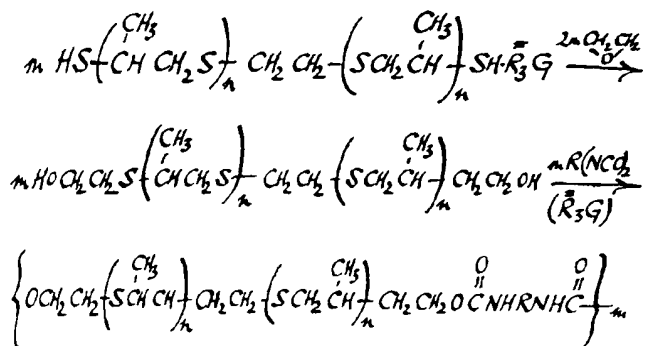


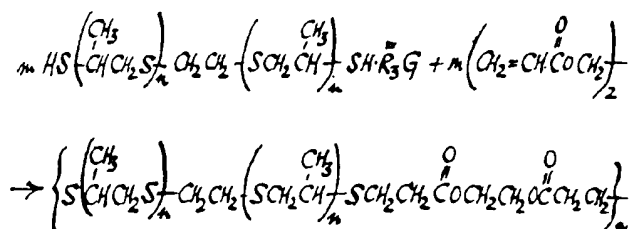
The polythioether thiol products of the present invention are useful polymers in the field of elastomers, coatings, adhesives and plastics applications. The secondary or tertiary rather than primary nature of the thiol groups of the present compositions is important in these applications. It results in a slower crosslinking, longer shelf life. The less reactive character of the novel compositions also allows their use as initiators for the free radical polymerization of vinylic monomers such as styrene.

Although the novel polythioether dithiols and polythiols are less reactive, they can be chain extended and/or crosslinked with known reagents for thiol groups to produce useful compositions. Suitable reagents include peroxides such as lead peroxide, epoxides such as diepoxides, polyunsaturates such as triacrylates, etc. The desirable degree of crosslinking, of course, is dependent on the intended field of application. A low degree of crosslinking results in highly elastomeric products, while highly crosslinked compositions behave as tough plastics.

The low molecular weight thioether thiols are useful as polymer additives and pesticides and intermediates for the same.

In several of the chain extension and crosslinking reactions, it is advantageous to use the amine complexes of the present polythioether dithiols and polythiols as produced. The reaction of the thiol groups with epoxides, isocyanates, acrylates, maleates is catalyzed by amines. The same amines used in the present episulfide ring opening reaction of thiols are effective for the subsequent chain extension and crosslinking reactions. The reaction conditions are also the same. As illustrative examples, for the chain extension of the present polythioether dithiols the following reaction schemes are given:





For other reactions, such as oxidation by peroxides, the amine is best neutralized or/and removed.

5 Since the catalyst polymer complexes are unstable at elevated temperatures, e.g., above 120°C., the polymer may be readily recovered by stripping off the catalyst at temperatures of about 20° to about 150°C., preferably at about 50 to about 120°C. It is preferred that the stripping operation be carried out at reduced pressures, preferably about 1 to about 500 mm Hg, more preferably about 10 to about 200 mm Hg.

10 Alternatively, the catalyst may be removed by mild acidification of the polymer-catalyst complex followed by extraction, e.g. with water. Suitable acids which may be used as carbon dioxide, carboxylic acids such as acetic acid, inorganic acids such as HCl, H₂SO₄, BF₃. Preferably, the acid is used in stoichiometric amounts based on the catalyst or in the case of weak acids it can be also used in an excess of about 1 to about 50% above the amount equivalent to the amine catalyst, more preferably about 5 to about 10% excess.

15 In general, the vulcanization of the free polythioether polythiols can be accomplished by the methods used for polysulfide polymers. For a detailed description of these methods see *High Polymers*, Vol. XII, part III, edited by N. Gaylord and published by the Interscience Division of J. Wiley & Sons (1962) incorporated herein by reference.

20 The advantages of the process and the resulting compositions of this invention may be more readily appreciated by reference to the following examples. It is noted that in these examples the CH₃ group is abbreviated as Me for the sake of brevity.

25 EXAMPLE 1

To 1.9 g. (0.05M) of trimethyl phosphine in a Pyrex tube, 20.0 g. (0.42m) methanethiol and then 18.8 g. propylene sulfide were condensed at about -70°C. (The word Pyrex is a registered Trade Mark). The closed contents were mixed and then allowed to come to 12°C. After being stirred for 72 hours at that temperature to complete the reaction, the unreacted components were removed under 30 mm pressure by film evaporation. The yellow liquid residual product weighed 26 g. and according to nmr, consisted mainly of the expected monoadduct product, i.e. 1-methylthio-2-propanethiol.

35 On fractional distillation of the crude product, 1 g. of crystalline trimethylphosphine sulfide byproduct was isolated. During the distillation some decomposition and a darkening of the residual mixture were observed.

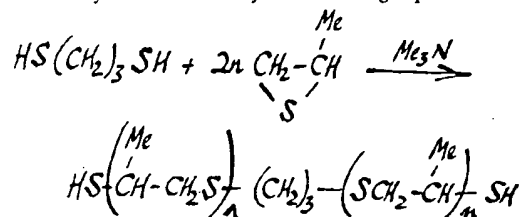
EXAMPLE 2

40 To a mixture of 5.4 g. (0.05m) trimethylenedithiol and 111 g. (1.5m) propylene episulfide placed in a dry ice-acetone cooled flask, 10 g. (0.1m) triethylamine was added. The resulting homogeneous mixture was left to stand at room temperature overnight. However, no reaction occurred; nmr examination of a sample showed the episulfide monomer to be unchanged.

45 To the above mixture, 5.9 g. (0.1m) of trimethylamine was added which started an exothermic reaction. In five hours, the temperature of the mixture rose to 70°C. The mixture was then cooled to room temperature to control the reaction and allowed to stand there overnight.

50 Examination of the resulting viscous liquid product by nmr showed that essentially all the propylene episulfide has been polymerized. The crude polymeric product was purged with nitrogen in vacuo to remove all the volatile impurities. Removal was completed by finally heating the product at 130°C. under 0.05 mm pres-

sure for 2 hours. The residual product, 112 g. (96% yield), was a colorless viscous oil. The reaction may be described by the following equation:



The number average molecular weight of the product was determined using a vapor pressure osmometer in benzene solution at 37°C. It was found to be 2211, indicating the presence of approximately 29 monomer units in the macromolecule. Assuming a complete conversion of the monomer, the stoichiometry of the reactants should lead to a polymer containing 30 monomer units.

The thiol functionality of the polymer was analyzed using the Zerewitinoff method for the determination of active hydrogen atoms. Calculation on the basis of the molecular weight found indicated 2.1 thiol groups per macromolecule, i.e., a thiol functionality of 2.1. The theoretical thiol functionality of the product is 2.0.

A liquid mixture of 11.64 g. (0.005m) polythioetherdithiol thus prepared and 9 g. (0.15m) ethylene episulfide was allowed to react in the presence of trimethylamine at room temperature over the weekend. A solid product resulted whose high temperature (150°C) nmr in dichlorobenzene indicated the presence of an about equal number of propylenesulfide and ethylenesulfide polymer units. Five grams of the product was recrystallized from 160°C. o-dichlorobenzene, washed with methanol and dried 3.8g. of purified copolymer. The nmr spectrum of this polymer was virtually identical with that of the crude product.

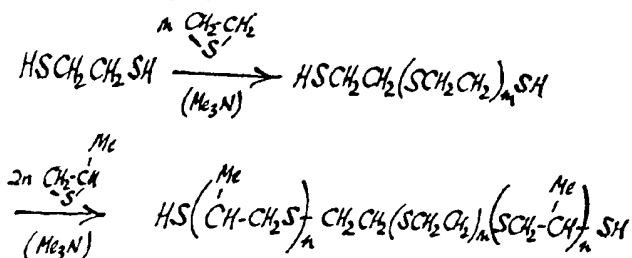
The product had the general formula:



Reaction of Dithiols with Episulfides to Form Block Copolymers

EXAMPLE 3

A block copolymer was prepared by reacting ethanedithiol with ethylene sulfide and propylene sulfide in the presence of trimethylamine. The reaction may be described by the following equation:



The experiment was carried out in the following manner:

To a stirred mixture of 0.94 g. (0.01m) ethanedithiol and 1.18 g. (0.02m) trimethylamine, an episulfide mixture consisting of 3.0 (0.05m) ethylene episulfide and 8.88 g. (0.12m) propylene episulfide was added in small increments. After the addition of the first 2-3 g., the temperature rose to 60°C. The mixture was cooled by dry ice-acetone. Nevertheless, subsequent additions repeatedly resulted in temperatures as high as 100°C. Nmr of a sample, taken immediately after the completion indicated that essentially all of the ethylene episulfide has reacted while more than half of the propylene episulfide was unconverted. Two hours after addition,

both episulfides were essentially all converted and a colourless, viscous liquid product was formed. After the removal of the volatiles the product had a molecular weight of 1194. Assuming a complete conversion of both episulfides the stoichiometry of the copolymerization should give a calculated molecular weight of 1282.

Analyses calculated for:
 $\text{HS}[\text{CH}(\text{CH}_3)\text{CH}_2\text{S}]_n(\text{SCH}_2\text{CH}_2)_m[\text{CH}_2\text{CH}(\text{CH}_3)\text{S}]_p\text{H}$, $\text{C}_{44}\text{H}_{88}\text{S}_{10}$: C, 44.88; H, 7.96; S, 47.43. Found: C, 45.18; H, 7.78; S, 47.32.

The secondary thiol groups of the compounds are surprisingly suitable for crosslinking reactions with reagents known for the crosslinking of dithiols and polythiols having primary thiol groups. Due to the lower reactivity of the secondary thiols, crosslinkable compounds can be prepared having extended pot life as compared to primary thiol compositions.

WHAT WE CLAIM IS:—

1. A process for preparing a thiol terminated thioether compound which comprises reacting at least one episulphide with hydrogen sulphide or an organic thiol or a mixture thereof, in the presence of an organic phosphine as catalyst.

2. A process according to claim 1 wherein the catalyst is a compound having the general formula R_3P wherein R is hydrogen, a C_1 to C_{30} hydrocarbyl radical or C_1 to C_{30} substituted hydrocarbyl radical.

3. A process according to either of claims 1 and 2 wherein the organic thiol has the general formula $\text{R}(\text{SH})_m$ wherein R is a hydrocarbyl radical or substituted hydrocarbyl radical of C_1 to C_{30} carbon atoms and m is 1 to 10.

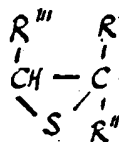
4. A process according to either of claims 1 and 2 wherein the organic thiol has the general formula $\text{R}(\text{SH})_m$ wherein R is a C_1 to C_{10} aliphatic hydrocarbon radical and m is 1 to 4.

5. A process according to either of claims 1 and 2 wherein the organic thiol is a C_1 to C_{30} hydrocarbyl dithiol or a C_1 to C_{30} substituted hydrocarbyl dithiol.

6. A process according to either of claims 1 and 2 wherein the organic thiol is a C_2 to C_6 alkylene dithiol.

7. A process according to claim 6 wherein the organic thiol is ethane dithiol.

8. A process according to any one of the preceding claims wherein episulphide has the general formula:



wherein R', R'' and R''' are hydrogen, hydrocarbyl radicals or substituted hydrocarbyl radicals.

9. A process according to claim 8 wherein the episulphide is an unsymmetrical episulphide.

10. A process according to claim 9 wherein the unsymmetrical episulphide is a mono-substituted episulphide.

11. A process according to claim 10 wherein R'' and R''' are hydrogen and R' is a C_1 to C_6 alkyl or cycloalkyl radical.

12. A process according to any one of claims 1 to 8 wherein the episulphide is ethylene sulphide or propylene sulphide.

13. A process according to any one of claims 1 to 7 wherein at least two different episulphides are reacted with hydrogen sulphide or the organic thiol.

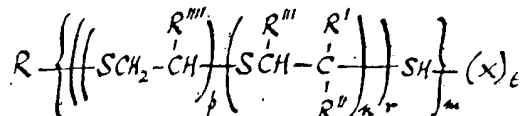
14. A process according to claim 13 wherein the reaction is carried out sequentially by adding a first episulphide to the reaction mixture; allowing the reaction to go substantially to completion; and thereafter adding a second episulphide to the reaction mixture.

15. A process according to claim 14 wherein the episulphides are ethylene episulphide and propylene episulphide and the organic thiol is ethane dithiol.

16. A process for preparing a thiol terminated thio-ether compound according to claim 1 substantially as hereinbefore described with reference to the Examples.

17. A thiol-terminated thiol ether whenever prepared by a process according to any one of the preceding claims.

18. A polythioether thiol compound having the general formula:



wherein R is a C_1 to $C_{20,000}$ organic radical; m is the valency of said radical; R' is a C_1 to $C_{20,000}$ hydrocarbyl or substituted hydrocarbyl radical; R'', R''' and R'''' are each independently hydrogen, a C_1 to C_{40} hydrocarbyl radical or a C_1 to C_{40} substituted hydrocarbyl radical; X is an organoamine or an organophosphine; p is 1 to 20,000, m is an integer, n is an integer of 1 to 50,000, r is an integer of 1 to 10, and t is 0 to 10; provided that if R'' is hydrogen R''' is also hydrogen, and also that when both R'' and R''' are hydrogen R' cannot be the same as R''''.

19. A polyether thiol according to claim 18 wherein X is a tertiary organoamine

having the general formula NR_s wherein R is a C_1 to C_{40} hydrocarbyl radical or a C_1 to C_{40} substituted hydrocarbyl radical and s is an integer of 1, 2 or 3.

20. A polyether thiol according to either of claims 18 and 19 wherein R is a C_1 to $C_{10,000}$ organic radical; m is 2 to 10; R'''' is hydrogen or a C_1 to C_4 aliphatic hydrocarbon radical; R' is a C_1 to C_4 hydrocarbyl radical; R'' and R''' are hydrogen; p is 1 to 1000; and t is 0 to 3.

21. A polyether thiol according to claim 18 wherein R is a C_1 to C_{40} aliphatic hydrocarbyl radical; R' is a C_1 to C_4 alkyl radical, allyl or propargyl; R'', R''' and R'''' are hydrogen; m is 2 or 3; p is 1 to 10,000; n is 2 to 3000; r is 2 or 3 and t is 0 to 3.

22. A polyether thiol according to claim 18 wherein R is a C_2 to C_{42} hydrocarbyl radical; R' is methyl, R'', R''' and R'''' are hydrogen; m is 2 or 3; n is 1 to 20,000 and p is 1 to 1000 and t is 0.

23. A polyether thiol according to any one of claims 18 to 20 wherein R is a heterocyclic organic radical containing sulphur or oxygen.

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